The Role of AsF_5 in Modifying the Electrical Properties of Polyacetylene, $(CH)_x$

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Summary In contrast to previous results we present evidence that AsF_5 reacts with polyacetylene to oxidize the $(CH)_x$ chains, in analogy with other acceptors, and to form AsF_6^- anions, which intercalate between the polyolefinic cation chains.

THREE principal mechanisms may be considered for the reaction of AsF_5 with $(CH)_x$ leading to the dramatic increase in electrical conductivity[1] which spans the range from insulator to metal depending upon the extent of AsF_5 uptake. These mechanisms are summarized in reactions (1)—(3).

$$(CH)_x + AsF_5 \longrightarrow (CH)_x^{\delta+} + (AsF_5)^{\delta-} \qquad (1)$$

$$(CH)_x + AsF_5 \longrightarrow (CH)_x^{+} + AsF_5^{-} \qquad (2)$$

$$2(CH)_x + 3AsF_5 \longrightarrow 2(CH)_x^{+} + 2AsF_6^{-} + AsF_3 \qquad (3)$$

Elemental analysis[2] and photoelectron spectroscopy[3] have provided evidence which has been interpreted in terms of reaction (1) or (2) in which the AsF_5 unit remains intact.

In this communication we present X-ray absorption, i.r., and other evidence for the third mechanism summarized in reaction (3). This mechanism is closely analogous to that demonstrated by Bartlett *et al.*[4] for AsF_6–graphite intercalation compounds. Preliminary X-ray absorption data for AsF_5 treated $(CH)_x$ are presented in the Figure, details

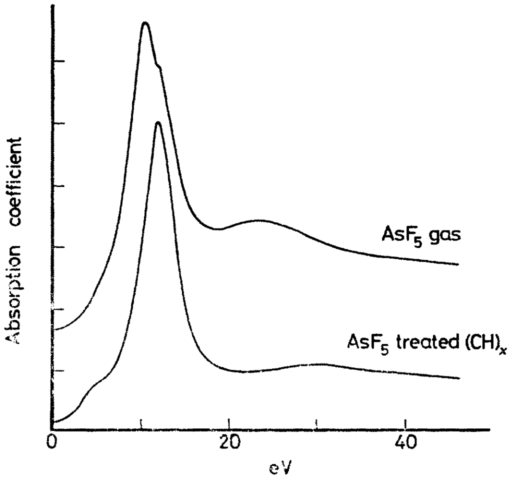

FIGURE. X-Ray absorption spectrum of AsF_5 treated $(CH)_x$.

of which will be published elsewhere.[5] The Figure shows As *K*-edge absorption data for polyacetylene containing *ca.* 10 atom % of As; similar absorption data for AsF_5 gas are also shown for comparison. The 1·4 eV shift between the AsF_5 gas and the arsenic species in $(CH)_x$ is identical to that reported for AsF_6^- in graphite. In addition, the shoulder located 6·7 eV below the AsF_6^- peak in doped polyacetylene occurs in the same position as the peak identified by Bartlett *et al.* as AsF_3. Detailed calculations of the various excitonic transitions in AsF_5, AsF_3, and AsF_6^- have been performed and will be published elsewhere.[6] The calculations suggest a core level structure broadened by core hole lifetime and instrumental broadening which may complicate the simple interpretation given here. The relatively weaker As^{3+} excitonic features are consistent with our observation that AsF_3 vapour is only weakly bonded to $(CH)_x$ and may be removed by pumping.[7] The presence of AsF_6^- in the AsF_5 treated $(CH)_x$ has been confirmed by i.r. transmission on thin films and also by reflection studies on thicker films. Both sets of data show strong peaks at 696 and 393 cm^{-1} characteristic of AsF_6^-.

Thus our model involves intercalation of AsF_6^- ions between the $(CH)_x$ chains in a similar manner to that described by Hsu *et al.*[8] for iodine treated $(CH)_x$. The separation of the (100) planes increases from 7·60 to 8·83 Å on intercalation[9] indicating a van der Waals diameter of 4·98 Å for AsF_6^-. Despite this increase in unit cell volume, scanning electron microscopy shows that the dimensions of individual fibres of $(CH)_x$ do not change on treatment with AsF_5. Although polyacetylene films have been shown to have a flotation density close to theoretical,[10] it must be assumed that the individual fibres are not single crystals but contain significant voids to allow the observed unit cell expansion without exhibiting macroscopic changes in dimensions. Electron diffraction studies confirm that the fibres are not single crystals. Simple calculation shows that the maximum AsF_6^- which could be accommodated in a monolayer around the outside of the 200 Å fibres would correspond to a composition $CH(AsF_6)_{0\cdot02}$. The observation of significantly higher doping levels is consistent with the intercalation model presented above.

We thank O.N.R. for partial financial support, the Stanford Synchrotron Laboratory for *X*-ray absorption facility, and the United States Department of Energy for co-operation.

(*Received, 29th December* 1978; *Com.* 1387.)

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